On the Effect of Concentration on the Spectra of Luminous Gases.

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It is now more than forty years since Lockyer* made the remarkable observation that in the spectra of electric spark discharges in mixtures of nitrogen and oxygen, the nitrogen lines were narrow and the oxygen lines broad when the oxygen was present in excess, and in the same way the oxygen lines were narrow and the nitrogen lines broad when the nitrogen was in excess. Although Lockyer put this discovery to practical use in order to make accurate measurements of the wave-lengths of the lines, it seems to have been relegated since to the numerous phenomena in spectroscopy which defy an explanation. Effects akin to this are by no means uncommon. It has long been known that the widths of spectrum lines from flames containing sodium or lithium are greatly affected by the concentration of these substances in the flame. Lord Rayleigh† remarks, in connection with the behaviour of the D lines of sodium in the Bunsen flame, "Is there no distinction in kind between encounters first of two sodium atoms and secondly of one sodium atom and an atom, say, of nitrogen? The behaviour of soda flames shows that there is. Otherwise it seems impossible to explain the great effect of relatively very small additions of soda in presence of large quantities of other gases. The phenomena suggest that the failure of the least coloured flames to give so high an interference as is calculated from Doppler's principle may be due to encounters with other gases, but that the rapid falling off when the supply of soda is increased is due to something special. This might be of a quasi-chemical character, *e.g.*, to temporary associations of atoms, or again to vibrators in close proximity putting one another out of tune."

Since these words were written our knowledge of the circumstances which govern the widths of broadened spectrum lines under certain specified conditions has materially increased. Stark's suggestion,‡ that the broadening of the lines in the spectra of condensed spark discharges is intimately connected with the resolution of the lines into components by the electric field, has been fully confirmed, and it has been shown that in the case of hydrogen and helium the broadening observed under these conditions can be accounted for satisfactorily and completely by the resolution of the lines by

* 'Phil. Mag.' [5], vol. 6, p. 161 (1878).

† 'Phil. Mag.' [6], vol. 29, p. 274 (1915).

‡ 'Elektrische Spectralanalyse Chemischer Atome,' 1914.

the electric fields of neighbouring charged particles on the radiating atoms.* The electrical resolution of the lines of hydrogen and helium has been examined by a number of observers, and reliable data, both qualitative and quantitative, are available; in the case of other elements, though considerable progress has been made, our information is less cemplete, but it is known that for a given electric field the resolution of the lines of heavier atoms such as sodium is very small in comparison with that of the hydrogen or helium lines. It is difficult, therefore, to account for the behaviour of the lines of sodium and many other lines of heavy elements which broaden easily to an extent which seems quite out of proportion to their electrical resolution.

Phenomena depending on the concentration of the radiating atoms are well exhibited in the case of the spectrum of lithium. Lecoq† has shown that the relative intensities of lines of the principal and the subordinate series are greatly affected by the concentration of lithium salt in a solution when the spectrum of sparks from the surface of the solution is examined, the subordinate series being relatively enhanced at higher concentrations. More recently Konen and Hagenbach‡ and Saunders§ have observed new combination series in the spectrum of lithium in electric arcs in which the concentration of lithium vapour was very great, and King|| has shown that the lithium line $\lambda = 6708$ A, which in sources containing very little lithium vapour appears as a close doublet, develops a new component when the concentration of lithium in the source is increased. Lockyer's "long lines," which are also the last lines to disappear from the spectrum of a substance when the concentration of that substance in the source is diminished, are another example of the same phenomenon, which thus appears to be perfectly general. Two other phenomena may be mentioned. The pole effect, or the small changes in the wave-lengths of certain lines in the neighbourhood of the poles of the electric arc, has been considered by Royds¶ to be connected with the increase in the concentration of the radiating atoms in this region, and, lastly, Burns** has found that certain manganese lines occurring as impurities in the iron arc differ in wave-length from the lines given by a manganese salt in the carbon arc, some barium lines being affected in the same way. Bilham†† has investi-

* Nicholson and Merton, 'Phil. Trans.,' A, vol. 216, p. 459 (1916); Merton, 'Roy. Soc. Proc.,' A, vol. 92, p. 322 (1916), and vol. 95, p. 30 (1918).

† 'Spectres Lumineux,' p. 56, Paris, 1874.

‡ 'Phys. Zeitschr.,' vol. 4, pp. 592, 801 (1903).

§ 'Astrophys. Journ.,' vol. 20, p. 188 (1904).

|| 'Astrophys. Journ.,' vol. 44, p. 169 (1916).

¶ 'Astrophys. Journ.,' vol. 41, p. 154 (1915).

** 'Comptes Rendus,' vol. 156, p. 1976 (1913).

†† 'Astrophys. Journ.,' vol. 42, p. 469 (1915).

gated a similar case. It thus appears that in certain cases the three phenomena of broadening, variations in the relative intensities of the lines, and changes in wave-length are intimately connected with the concentration of the radiating atoms in the source.

I have carried out a number of experiments with a view to discovering whether the phenomena of broadening and enhancement of certain lines in the case of sodium and lithium can be referred to a quasi-chemical effect in accordance with one of the suggestions of Rayleigh (*loc. cit.*). When the chemical similarity of sodium and lithium are considered, it seems extremely probable that if temporary associations of two sodium atoms or two lithium atoms occur in luminous sources, there will also be temporary associations of sodium atoms with lithium atoms. It would be expected that the addition of a large quantity of lithium to a source containing a small quantity of sodium would result in a broadening of the sodium lines, and similarly the addition of a large quantity of sodium to a source containing very little lithium should broaden the lithium lines, enhance the subordinate series relatively to the principal series, and change the doublet $\lambda = 6708$ A. into a triplet. I was unable to obtain a lithium salt sufficiently free from contamination with sodium to examine the effect of the addition of lithium to sources containing sodium, but the converse experiment was carried out without difficulty, both in the case of flames and with arc spectra *in vacuo*. In neither case could any change be detected. With an arc burning between very pure carbon poles, at a pressure of a few millimetres, the phenomena described by King (*loc. cit.*) could be seen clearly when the carbons were treated with dilute solutions of lithium nitrate. The spectrum was observed with a Lummer-Gehrcke plate, crossed with a Hilger constant-deviation spectroscope, and the change of the doublet into a triplet when the quantity of lithium in the source was increased was very striking; but the addition of large quantities of soda produced no such change, nor were the subordinate series enhanced. These experiments seem to exclude temporary associations of atoms, in the chemical sense, as the explanation of the phenomena, but since all the evidence points to a specific influence of atoms of the same kind on one another, it seemed that more decisive results might be obtained from a study of the mutual influence of atoms of hydrogen and helium on one another since in this case we have accurate information of the electrical resolution of the lines.

In the previous investigation,* in which a study was made of the broadening of the lines of helium by condensed discharges, not only were the structures of the broadened lines in complete harmony with their electrical

* Merton, *loc. cit.*, 1918.

resolutions, but a further proof of the existence of powerful electric fields under these conditions was afforded by the presence of the combination series observed by Koch,* and other combination lines which, when the spectrum is excited by uncondensed discharges, are only found in those regions of the discharge tube where the potential gradient is very great. The aforementioned phenomena relating to the effect of the concentration of charged particles lead one to enquire whether, in the broadening of helium lines and hydrogen lines in vacuum tubes, which is definitely due to the electrical resolution, the electric fields which are operative are simply those which are due to the proximity of any charged particles to the radiating atoms, or whether there is something specific in the magnitude of the electrical resolutions produced by the proximity of charged particles of the same kind.

In order to investigate this, a study has been made of the broadening of the helium and hydrogen lines in vacuum tubes containing these gases in varying proportions. The vacuum tubes were of the usual H pattern, and were provided with side tubes, into which were sealed short lengths of platinum tube, connected with palladium tubes, which were closed at the other end; the quantity of hydrogen in the tubes could thus be controlled by heating the palladium tube in a current of hydrogen or in a hydrogen flame, or, alternatively, in an atmosphere free from hydrogen. The most interesting results in the case of helium were obtained with a tube which was filled with helium at a high pressure, the greatest care being taken to exclude impurities; the precise pressure in this tube was not measured, as it was particularly desired to exclude the possibility of contamination with mercury, but, from previous experience and comparison with other tubes in which the pressure had been measured, it may be stated that the pressure was greater than 50 mm. of mercury. The last traces of hydrogen were removed through the palladium tube. The tube was excited by an induction coil with an adjustable spark gap in series, and, by means of a high tension switch, a large condenser could be put in parallel with the terminals of the induction coil. The spectra were observed with a constant-deviation spectroscope, and photographs were taken with a camera attached to this instrument. With a small spark gap and the condenser in parallel, the lines were found to be enormously broadened, in accordance with their electrical resolution; the Koch (*loc. cit.*) series was strong, and combination lines were observed at $\lambda\lambda$ 6635, 4911, 5043 A., of which the line $\lambda = 5043$ A.† does not appear to have been observed before. These lines, which were measured approximately, were sharp on one edge and diffuse on the other, indicating the

* 'Ann. d. Phys.,' vol. 48, p. 98 (1915).

† *Cf.* Saunders, *loc. cit.*

unsymmetrical nature of their electrical resolution, but the spark line at $\lambda = 4686$ A. was not observed with certainty, owing, no doubt, to the fact that the electrical resolution of this line is symmetrical, and it would therefore be so diffuse as to escape notice. On admitting a small trace of hydrogen, the current through the primary of the coil and the length of the spark gap being kept constant, the helium lines were broadened as before, but the hydrogen lines $H\alpha$, $H\beta$, and $H\gamma$ appeared to be perfectly sharp though faint. On further increasing the amount of hydrogen in the tube, the hydrogen lines began to show signs of diffuseness, and, with a large quantity of hydrogen, they became definitely broadened.

These observations were made both side-on and end-on with similar results, excepting that, for a given concentration of hydrogen, the Balmer lines were relatively more intense when the tube was viewed end-on. This follows from Curtis'* observation, that in helium tubes containing a small trace of hydrogen, the Balmer lines could only be detected just outside the capillary, when a condenser and a small spark gap were included in the circuit. For this reason, reliance could not be placed on the end-on observations alone, for in this case the Balmer lines might have their origin just outside the capillary, where the current density would be smaller; but the photographs taken side-on showed the same effect. When discharges of the same intensity were passed through tubes containing pure hydrogen, the Balmer lines were very broad, whilst tubes containing hydrogen and helium in similar proportions gave broadened lines for both elements. The electrical resolution of the diffuse series of helium is less than that of the Balmer lines of equal term-number; thus, using Stark's (*loc. cit.*) results, we should expect the broadening of the line $H\beta$ to be very nearly twice as great as that of the helium line $\lambda = 4471$ A. The fact that the latter line is broad and $H\beta$ is narrow when the amount of hydrogen present is very small, seems to show that there is in this case a specific action of charged atoms of the same kind on one another, and that the resolution produced by a neighbouring charged atom of the same kind is vastly greater than that produced by a charged atom of another kind. These observations are in agreement with those of Lockyer, but they are made in a case in which there can be little doubt as to the ultimate cause of the broadening.

In repeating Curtis' (*loc. cit.*) observations, which have been referred to above, a very curious fact was noticed. When the high-pressure helium tube containing a little hydrogen was excited by an uncondensed discharge and observed through a direct vision prism, the lines of both hydrogen and helium were of uniform intensity throughout the capillary. On putting in

* 'Roy. Soc. Proc.,' A, vol. 89, 146 (1914).

the condenser and a small spark gap, the hydrogen lines became relatively much weaker in the capillary, but showed fairly brightly just at the ends, in accordance with Curtis' observation. When, however, the condenser was cut out again, the hydrogen lines did not immediately reappear in the capillary with uniform brightness, but were seen as bright spots at the ends of the capillary, these bright spots gradually extending until the intensity was uniform, which did not, as a rule, occur until about 30 seconds after the condenser had been cut out. Putting in the condenser for a few seconds only showed the effect to a much smaller extent. The bright spots of the Balmer lines seemed to spread into the capillary in a manner which strongly suggested a diffusion of the gas, and they spread at very much the same rate and with the same general appearance as when a small quantity of hydrogen was let into the tube (previously freed from that gas) whilst the discharge was running. It looks as if the weakening of the Balmer lines in the capillary when the condenser is put in the circuit is due to the fact that the hydrogen is in some way driven out of the capillary into the bulbs by the action of the discharge.

There are many cases in which the relative intensities of the lines in a mixture of two gases is radically altered by the inclusion of a condenser and spark-gap in the electrical circuit. Such phenomena have usually been attributed to the changes in the electrical conditions, but in the light of the observations recorded above it seems by no means improbable that the ultimate cause is sometimes to be found in the alteration of the relative proportions of the gases in the capillary of the discharge tube.